Alkaline pulping in aqueous alcohols and amines

ABSTRACT
Addition of alcohols and amines during alkaline pulping increased the rate and selectivity of delignification above that of conventional soda and kraft processes. Although the pulps obtained at low amine charges possessed tear values superior to kraft pulps, they were lower in burst and tensile strengths. At high amine levels the alkali requirement was substantially reduced but, despite the higher hemicellulose stabilization and retention, the cellulose viscosity and pulp mechanical properties deteriorated. The preferential alkali adsorption and solvent effects influenced the structure of wood polymers and reaction kinetics in these systems, providing a unique but complex tool for studying the mechanism of base-catalyzed delignification of wood.

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There have been efforts to delignify wood by base-catalyzed solvolysis in organic solvents but, as in the soda process and in acid-catalyzed solvolytic delignification, the methods have been more effective for pulping hardwoods than softwoods (1-7). Among the various solvent systems investigated, however, the amine compounds fall into a unique category in substantially increasing the soda pulping rate of all wood species (8-11) and are the subject of renewed research efforts for developing a sulfur-free alkaline pulping system(12-17).

Although the physiochemical aspects of alkaline delignification in aqueous organic solvents are quite complex, these systems could provide new insight into the interaction and reactivity of cell wall polymers. The sorption of alkali and solvent, as well as the base ion activity in the solid phase influencing the comparative reactivity and degradation of lignin and polysaccharides, can be conveniently manipulated by changing the type and concentration of solvents There are certain solvolytic or nucleophilic substitution reactions that could be greatly influenced by the solvent system. For instance, in soda pulping with aqueous methanol it was proposed that partial methylation of benzylic hydroxyls is responsible for the prevention of lignin condensation and increased delignification rate (7).

The influence of amines in increasing the rate of β-0-4-ether cleavages of blocked phenolic units in lignin was reported earlier (16). In addition to this reaction, other chemical and physical effects undoubtedly account for the accelerated pulping in alkaline liquors and improved pulp strength. Furthermore, certain amines are known to cause intrafibrillar swelling of cellulose (18) which would modify the micro-

structure and papermaking properties of pulp fibers that have to be taken into account.

The effects of these solvents and sodium hydroxide concentration on the rate and selectivity of pulping southern pine were determined, and the changes occurring in the microstructure and properties of fibers are reported in this paper.

Results and discussion
Delignification rate and selectivity

As expected, the miscibility of the aqueous aliphatic alcohols and alkali solutions was found to be very critical with respect to the rate and selectivity as well as the

1. Delignification rates of southern pine in aqueous alcohols (1.5 *N* NaOH in 50% aqueous alcohols, liquor/wood = 10, 150° C). (□-MEA, ●-methyl cellosolve, ◇-MeOH, ☉-EtOH, ▲-PrOH, △-BuOH.)

uniformity of delignification of loblolly pine. A 1.5 *N* sodium hydroxide solution in 50% methanol, ethanol, and methyl cellosolve, for instance, formed single phases; and the rates and selectivities of delignification were about the same. (Figs. 1 and 2). On the other hand, the higher alcohols, n-propanol and n-butanol, being only partially miscible, formed two phases with different pulping rates leading to nonuniform pulping. Such immiscible mixtures would certainly make the alkali–wood interactions too complex for evaluating and interpreting the results with sufficient precision.

The pulping selectivity increased with increasing concentration of organic component and alkali (Figs. 3-5). The solvent concentration effect was particularly significant for the amino alcohol, monoethanolamine (MEA). These concentration factors are, of course, highly interdependent and complex, being governed by the properties of each organic compound involved. Moreover, the solubility, sorption, and catalytic activity of sodium hydroxide are influenced by the kind and concentration of the solvent, which determines the overall pulping rate in these mixtures.

in general, low-molecular weight mono- or di-functional amines were more effective than higher molecular weight or long-chain-length analogues; and primary amines were better than secondary amines, corroborating the earlier published data(14, 17). In addition to purely physical or solvation effects, their structures and reactivities with lignin in accelerating the pulping rate have to be taken into consideration. In this context, equal concentration of amine groups has to be the basis for comparing the solution of compounds with different amine equivalent
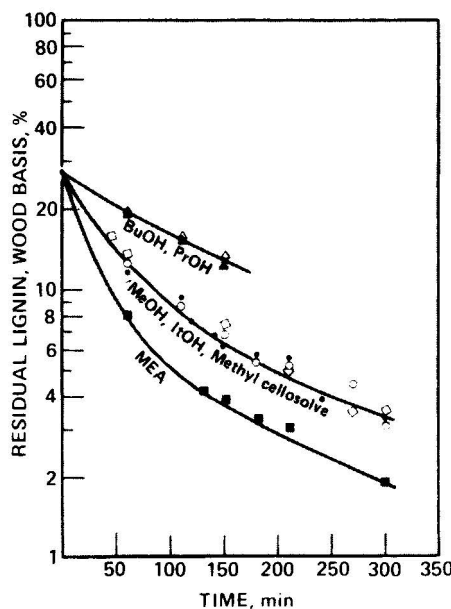
weights. Molar volume, bulkiness, and the hydrocarbon characteristics Influence greatly the ability of the solvent in wetting, swelling, and solvation of lignin and are major factors in determining the delignification rate.

Solubility and sorption of sodium hydroxide

The miscibility limit is reached upon raising the base or solvent concentrations in the liquor. The limit is different for each system and is determined by its phase diagram. It is interesting to note that high-boiling amines are commercially dehydrated with sodium hydroxide. As expected, the immiscible or two-phase systems with greatly varying chemical composition of aqueous and organic phases resulted in complex interactions with wood chips, leading to non-uniform pulping.

A 40-ml 0.6 N sodium hydroxide solution of 70% ethylenediamine (EDA), for instance, gave a barely discernible aqueous layer of 1.2 ml which was 16.3 N in sodium hydroxide while the organic phase was only 0.11 N. In 60% EDA the aqueous phase was 0.75 ml and 12.1 N, and the organic phase was 0.4 N in sodium hydroxide. With such liquors the uniform distribution of sodium hydroxide in and between chips would be impossible, resulting in shived pulps requiring overcooking for complete reduction to fiber. The solubility problem is further aggravated at elevated temperatures by the slow diffusion of alkali in the organic phase.

A more significant phenomenon governing the pulping rate is related to the adsorption of sodium hydroxide or imbibition of organic component by the wood polymers, even from a single-phase solution. Consequently, the large variability in the concentration and activity of the base in microscopic level would be a crucial factor in determining the overall rate processes. These aspects of the base-catalyzed solvent pulping have not been sufficiently recognized. A few examples of these factors were

evaluated to demonstrate the complexity of these systems.

Adsorption of sodium hydroxide by cellulose in aqueous alcohols has been extensively studied (18). The apparent adsorption increased with increasing concentration of base and alcohol. Under these conditions alkali swelling of cellulose is dependent on the degree of hydration of base: the smaller the dipolar hydrate size, the greater the penetration and lower the overall swelling. In the case of aqueous amine solutions of sodium hydroxide. the system is more complex because of the independent cellulose swelling capability of amines themselves.

The centrifugal liquid retention values (CLRV) and the alkali content of fiberized wood and wafers equilibrated overnight with various pulping liquors were determined as an indication of swelling and alkali sorption. The apparent sodium hydroxide normality of the liquor retained in the wood, compared with that of the free liquor,
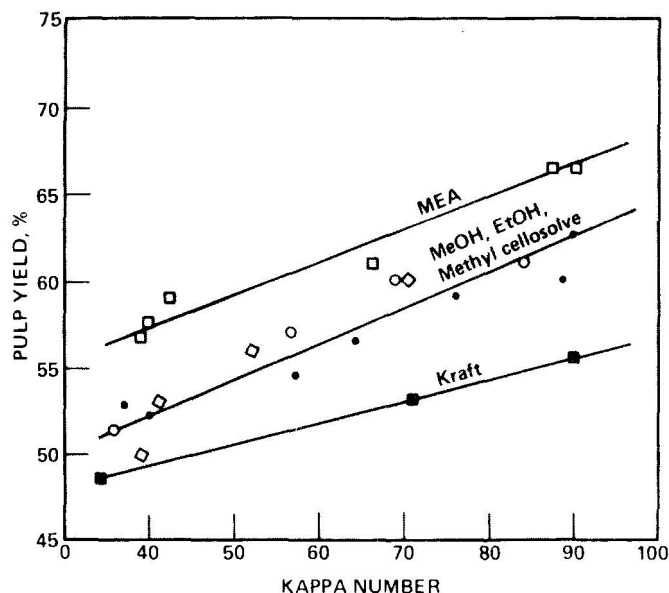
2. Delignification selectivity of southern pine in aqueous alcohols (1 5 N NaOH in 50% aqueous alcohols, liquor/wood = 10, 150° C, kraft: 25% sulfidity, 170°C) (□-MEA, ● methyl cellosolve, ◇-MeOH, ◉-EtOH, ■-kraft.)
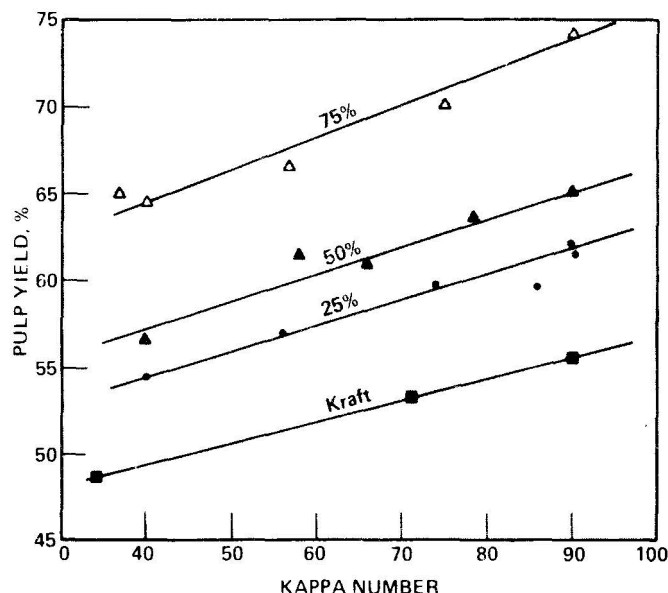
3. Effect of MEA concentration on the delignification selectivity of southern pine (1 5 N NaOH 160° C, liquor/wood 10, kraft 25% sulfidity, 170° C)
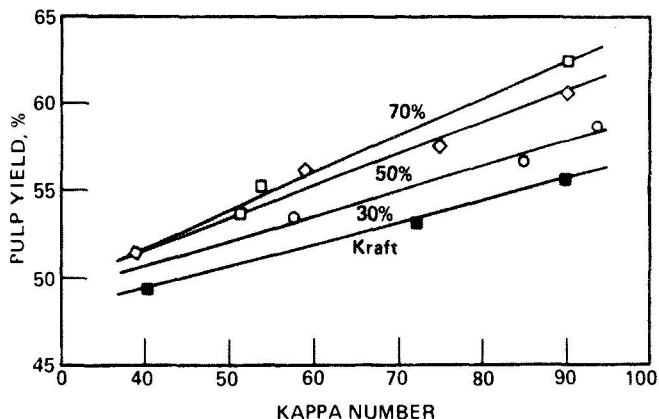
4. Effect of MeOH concentration on the delignification selectivity of southern pine (1.5 N NaOH, 150°C, liquor/wood = 10; kraft: 25% sulfidity, 170°C).
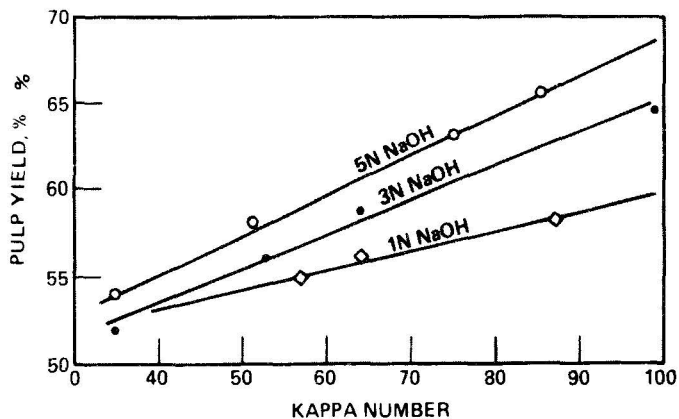
5. Effect of NaOH concentration on the delignification selectivity of southern pine in 50% MeOH (150° C, liquor/wood = 10)

varied dramatically with the type and the concentration of the organic component (Table I). As expected, some alkali loss occurred through neutralization with wood acids. Because of the difficulty in defining the microscopic composition and measuring the mean specific gravity, no attempt was made to calculate the volume of the retained liquor. Also, if it were not for the entrapment of free liquor, the true concentration of adsorbed alkali, as governed by the degree of hydration of sodium hydroxide, would be considerably higher. In comparison to **MEA,** high apparent sodium hydroxide

adsorption in EDA solutions would certainly account for the increased rate and lower alkali requirement found with this amine.

The preferential sorption and imbibition of organic component in various polymer phases in the fiber wall, particularly if it occurs in lignin, would improve the wetting, swelling, and accessibility thus accelerating the pulping. Such solvent effect may account for the ease of delignification of diazomethane-methylated wood in aqueous MEA and dioxane which was communicated earlier (*16*). Blocking of free phenolic groups by methylation

greatly reduced the pulping rate of loblolly pine in soda liquor largely because of the poor wetting and swelling of lignin and, to some extent, because of decreased cleavage rate of β-0-4 ether linkages of blocked phenolic units. It may be surmised that the preferential imbibition of MEA or dioxane could accelerate the cleavage of these blocked ether units because of improved wetting of lignin. The physical and chemical mechanisms of these unique solvent effects and their significance in wood delignification remain to be established.

Pulp properties

As in most alkaline processes, pulping with high alkali charges resulted in cellulose degradation and loss of pulp viscosity. Therefore, to determine the effect of solvent concentration on pulp properties the alkali charge was adjusted downward with increasing organic component using relatively constant cooking temperature and time (Table II). With the addition of the amines, MEA and EDA, the soda pulping rate increased and the pulps produced at the optimum liquor composition possessed higher tear but lower burst and tensile strengths than kraft pulps, corroborating the results obtained with black spruce by Kubes *et al. (14)*. This was particularly the case with EDA pulps. In comparison with the soda

I. Effect of liquor composition on NaOH adsorption and centrifugal liquid value (CLRV) of loblolly pine

Liquor composition	CLRV,[a] g/g	Concentration, NaOH in	
		Retained liquor, N	Free liquor, N
Wood wafers—10:1 liquid ratio			
Water, 0.875-N	1.01	0.74	0.79
50% EDA, 0.5-N	1.28	1.19	0.18
50% EDA, 1.0-N	1.34	2.59	0.43
Water, 4-N	1.89	3.66	3.77
Fiberized wood—20:1 liquid ratio			
Water	0.87	. . .	. . .
Water, 0.875-N	1.48	1.01	0.77
10% EDA, 0.875-N	1.43	0.84	0.77
35% EDA, 0.875-N	1.38	2.05	0.69
50% EDA, 0.875-N	1.25	4.10	0.53
50% MEA, 0.875-N	1.25	1.06	0.74
50% MeOH. 0.875-N	0.96	1.65	0.70

[a]Does not include NaOH.

II. Effect of amine concentration on pulp properties

Liquor composition	NaOH,[a] %	Temperature, °C	Time, min	Yield, %	Kappa no.	Viscosity, mPa·s	CSF, ml	Burst index, kPa·m²/g	Tear index, mN·m²/g	Tensile index, km	Density g/cm³
Loblolly pine											
Soda	30	170	240	42.5	33	9.5	350	5 49	15.6	8.1	0.65
Soda—50% MeOH	22	170	180	49.5	31	11.5	350	6 08	14.7	9.2	0.65
Soda—25% MEA	22	160	150	48.1	30	23.0	600	6 47	20.6	8.3	0.65
							350	6 57	18.9	8.8	0.66
Soda—50% MEA	22	160	90	55.4	30	24.0	600	5 69	19.3	7.7	0.61
							350	6 18	16.7	8.2	0.64
Soda—75% MEA	22	160	90	58.9	26	15.0	600	5 49	16.1	7.7	0.61
							350	5 78	14.7	8.2	0.64
Soda—90% MEA	17	160	90	60.2[b]	39	9.4	600	5 30	14.9	7.4	0.61
							350	6 08	11.7	9.2	0.64
Soda—10% EDA	24	160	90	50.1	46	28.0	600	5 69	24.7	8.3	0.62
							350	6 37	23.5	8.6	0.64
Soda—351 EDA	20	160	90	52.5	38	30.0	600	5 79	17.4	8.4	0.63
							350	6 47	15.9	9.0	0.65
Soda—55% EDA	15	160	90	57.5	43	5.2	600	5 49	13.6	8.0	0.62
							350	6 28	12.9	8.7	0.64
Soda—75% EDA	15	160	90	58.0[b]	32	5.0	600	4 02	13.0	6.6	0.58
							350	451	11.5	6.9	0.62
Kraft	18	170	90	47.5	33	30.0	600	7 75	14.3	10.4	0.66
							350	8 04	13.3	11.0	0.68
Kraft—10% EDA	14	170	90	50.0	28	22.0	600	6 47	18.6	8.8	0.62
							350	6 77	16.7	9.4	0.65
Kraft—35% EDA	12	160	90	51.0	36	23.0	600	5 30	20.3	7.8	0.62
							350	500	16.7	8.5	0.66
Balsam fir											
Kraft	18	170	90	44.7	32	. . .	600	10.30	12.3	13.1	0.73
							350	11.28	11.3	14.0	0.75
Kraft—35% EDA	12	160	90	50.7	42		600	8.33	12.5	11.1	0.71
							350	9.02	11.6	11.8	0.73
Soda—10% EDA	24	170	90	43.8	37		600	8.04	15.3	10.6	0.69
							350	8.53	15.2	11.4	0.72
Aspen											
Kraft	18	160	90	55.4	15	. . .	550	3.53	8.2	7.5	0.70
							350	6.57	8.7	10.7	0.76
Soda—10% EDA	24	160	90	53.2	16		550	3.14	10.3	6.4	0.68
							350	5.00	9.8	8.2	0.76

'Percent active alkali for kraft-EDA, 25% sulfidity; 4:1 LR for kraft control cooks, all others at 6:1   [b]Include shives.

III. Effect of amine concentration on the carbohydrate composition of loblolly pine pulps

Cooking liquor	Yield, %	Kappa no.	Reducing sugar anhydride, %	Carbohydrate composition, %				
				Galactose	Glucose	Mannose	Arabinose	Xylose
25% MEA	48.1	31	95.0	08	80.9	9.6	0.8	7.8
50% MEA	53.4	29	96.8	1.2	77.8	11.0	0.8	9.2
75% MEA	54.7	25	96.3	0.5	74.1	13.1	1.3	11.0
90% MEA	54.9	19	96.7	0.9	74.5	14.3	0.9	9.5
10% EDA	43.4	25	98.2	0.4	86.4	6.7	0.5	6.0
35% EDA	47.3	27	96.1	0.7	81.9	9.9	0.8	6.6
75% EDA	54.3	21	97.6	0.8	77.2	13.9	0.8	7.3
50% MeOH	49.5	31	94.8	0.6	80.0	6.8	1.0	11.7
Soda	42.5	33	94.1	0.5	85.7	6.9	0.5	6.4
Kraft	48.9	34	94.2	0.7	82.1	7.1	0.7	9.4

process, lower alkali charges and milder cooking conditions were required, resulting in higher yields of pulps with higher viscosities which indicates less cellulose depolymerization and more hemicellulose protection. A similar trend was also observed when amines were added to kraft cooks.

The yield and hemicellulose contents of the loblolly pine pulps increased largely because of improved protection of glucomannan in amine cooks and, interestingly, xylan in alcohol cooks (Table 111). At high amine levels the pulps contained more hemicelluloses but were lower in viscosity and easily hydrated during treatment in the PFI mill, developing poor strength. The increased accessibility accompanying the sorption of sodium hydroxide, as shown in Table I, presumably accelerated the chain scission in cellulose, resulting in the loss of viscosity and pulp strength.

The hemicellulose content and particularly the xylan content of EDA pulps obtained with low amine charges were lower, and the pulps possessed

6. Effect of EDA on cellulose structure in pulp and wood.

RELATIVE INTENSITY DISPLACED

Kraft
Wood
Kraft in 70% EDA
Wood in 50% EDA, 0.5 N NaOH
Wood in 50% EDA, 1.0 NaOH

DIFFRACTOMETER ANGLE, 2θ, degrees

very high tearing resistance. The stripping of xylan from fiber surfaces could lead to interfiber and intrafiber debonding and higher tear values. The strength results obtained with balsam fir and aspen were essentially similar to the loblolly pine data. The spent liquors from soda–EDA (35%) and kraft–EDA (35%) pine cooks contained 4.0 and 5.2% xylan, respectively, and equal amounts of glucan oligomers (2.5% on wood basis). The values are 5 to 6 times those found in kraft spent liquors. In general, the capability of amines to stabilize hemicelluloses towards alkaline peeling reaction was indicated—a fact that one would anticipate from the well-known reactions of amines with carbonyls and reducing sugars. In addition, more efficient stabilization of polysaccharides towards peeling can be attributed to the high alkali concentration (19,20) that would develop as a consequence of adsorption of sodium hydroxide by the wood early in the cook.

The increased decrystallization and disorder in cellulose structure when wood is exposed to sodium hydroxide solutions in high concentrations of EDA and MEA could occur and contribute to poor mechanical properties of the pulp fibers. The increased disorder in the cellulose structure of wood and kraft pulps treated with EDA solutions was indicated by their X-ray diffraction patterns (Fig. 6). The solution of 0.5 N and 1.0 N sodium hydroxide in 60% EDA caused decrystallization of wood cellulose, while an amine cellulose formation is indicated for kraft pulp in 70% EDA. Such physical changes would be expected to cause the development of stress concentrations in the fiber wall and result in the loss of mechanical strength. This loss would be in addition to the weakening of fiber caused by concomitant cellulose depolymerization and lowering of viscosity during pulping.

Amine reactions with wood components

Because of the accelerated pulping rate the soda–amine system is being reevaluated in conjunction with the

development of a sulfur-free pulping process. A unique aspect of this system, however, is concerned with the delignification mechanism involved and the specific reactions of amines in accelerating the cleavage of β-0-4 ether bonds in blocked phenolic units in lignin, as discussed earlier (16). The possibility of the Mannich reaction, involving formaldehyde generated via reverse aldol cleavage of the γ-carbon from the quinonemethide intermediates in lignin and subsequent blocking of the five-position of free phenolic units, has also been proposed (21). This reaction could prevent lignin condensation thereby accelerating pulping; it is under further investigation.

The soda–amine pulps contained 0.1 to 0.2% nitrogen which is undoubtedly attached mostly to lignin and reducing end-groups of carbohydrates. These groups could, to a small extent influence the surface charge and papermaking properties of these pulp fibers. The lignins isolated from the soda–amine spent liquors contained 2 to 3% nitrogen. The nonvolatile solids in the spent liquors contained 8 to 10% nitrogen, ash-free basis. Although such large chemical losses preclude any practical application of the method, the system offers a useful tool for studying wood delignification and for modifying the physical structure and reactivity of wood components.

Conclusions

The rate and selectivity of alkaline delignification in aqueous alcohols and amines increase with increasing concentration of alkali and organic component. At high solvent additions the sodium hydroxide adsorbed by the wood causes the effective alkali concentration in the chips to increase, thereby contributing to the increased pulping rate while it also accelerates the depolymerization of cellulose, lowering the pulp viscosity. The increased alkali concentration favors the carbohydrate stabilization by affording protection against end-group peeling, thus improving the hemicellulose retention.

The preferential sorption and imbibition of organic component by the cell wall polymers may cause improved wetting and swelling and influence the rates of certain key reactions, but verification of this effect requires development of a more precise experimental method.

Although the unusually high pulp tear obtained at low levels of amine addition is unique and of mechanistic interest, a viable organosolv process for improved pulping has to use solvents that can be more efficiently recycled and preferably demand much less alkali than required in these systems.
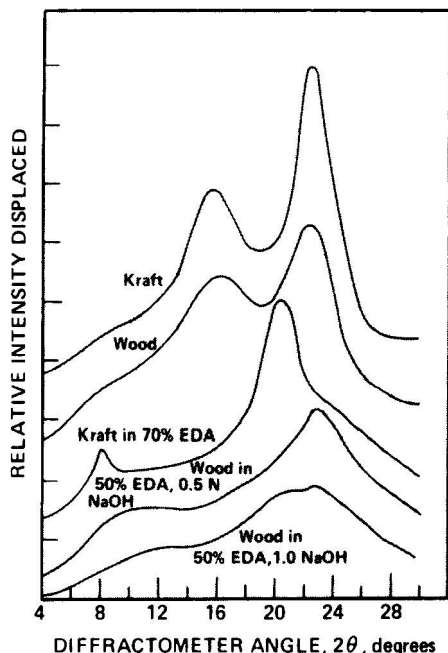
Experimental

Purified grade solvents (>98%) were used, and the various concentrations of aqueous solutions were prepared and reported as weight percent of solvent in the mixture.

The pulping experiments were carried out in 100- or 300-ml stainless steel reactors heated in an oil bath or in a rotating steam-heated digester. The cooked chips were lightly fiberized in a blender and then thoroughly washed with hot water.

The centrifugal liquid retention values (CLRV) of wood were determined by a method described by Scallan and Charles (22) using two-piece stainless sleeve (3.2-cm ID) in a centrifuge tube where the bottom of the upper sleeve was covered with a 100-mesh screen. One-gram samples of loblolly pine wafers (1-mm thick) or coarse fiberized and defloureti wood (700-m1 CSF) were vacuum-impregnated and soaked overnight at 20°C in the cooking liquors at 10:1 and 20:l wood to liquor ratio, respectively. After centrifuging for 30 min at a centrifugal force of approximately 920g, the material was directly weighed before and after washing and drying to determine the weight of liquor retained. The alkali in the wash liquor and in treating liquor was determined by titrating to pH 8.2 in the case of amine-free solutions and to pH 10 subsequent to adding excess formaldehyde to form Schiff bases in amine solutions. The apparent normality of the liquor was estimated assuming all the liquid fraction retained in the wood had a specific gravity of one. CLRV values were obtained by subtracting the weight of sodium hydroxide from the weight of the liquor retained.

Kappa number, CED viscosity, and handsheet strength tests (after beating in a PFI mill) were performed according to TAPPI standards.

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